

PATENT SPECIFICATION

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- (21) Application No. 50635/74 (22) Filed 22 Nov. 1974
- (31) Convention Application No. 426 438
- (32) Filed 20 Dec. 1973 in
- (33) United States of America (US)
- (44) Complete Specification published 8 Sept. 1977
- (51) INT CL² C09D 1/00; B32B 13/04, 15/04, 17/06; C09D 1/02
- (52) Index at acceptance
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588 648 668
 - C1A 13

(72) Inventor RONALD WENTWORTH BEERS



(54) QUICK-CURING WATER-RESISTANT SILICA- OR SILICATE-CONTAINING COATINGS AND PROCESS OF PREPARING SAME

(71) We, EXXON RESEARCH AND ENGINEERING COMPANY, a Corporation duly organised and existing under the laws of the State of Delaware, United States of America, of Linden, New Jersey, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

Water solutions of alkali silicates are commonly used binders in zinc-rich inorganic coatings. Some colloidal dispersions of silica

one or two hours after application and under less than desirable conditions such as 50°F. and 70—80% RH (relative humidity).

Under these adverse conditions, currently available, self-curing systems redissolve, causing failure of the coating and requiring reblasting and recoating. To avoid this problem, many users of these water based inorganic coatings have changed to using the solvent based, ethyl silicates because they cure by absorbing moisture from the air. U.S. 3,320,082, 3,180,746, and 3,130,061 are relevant prior art patents. However, the fire hazard and toxicity of the solvents are disadvantages.

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SPECIFICATION NO 1485169

By a direction given under Section 17 (1) of the Patents Act 1949 this application proceeded in the name of VENEZIANI ZONCA VERNICI S.p.A., a Body Corporate organised and existing under the laws of Italy, of Via Malaspina 8, Trieste, Italy.

THE PATENT OFFICE

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coatings are that the former requires about one month's exposure to the atmosphere before it will resist a heavy rain while the latter will resist a heavy rain after only about eight hours' exposure to the atmosphere depending on the ambient temperature and humidity. Therefore, in a relative sense, the sodium-lithium vehicle is self-curing.

However, in practice, especially in the marine industry which is a major user of these inorganic zinc-rich coatings, weather conditions are such that the coating must become completely resistant to rain, fog or extended periods of drizzle in a matter of only

would resist all conditions of early exposure down to 40°F.

Polymerization of silicates and colloidal silica increases as the pH drops until it reaches a maximum for most systems at a pH of 5—6. Alkali silicate solutions usually have a pH in the range of 10.5—11.5 due to the presence of fixed alkalis such as sodium, lithium or potassium.

As the system dries upon evaporation of the water, mobility of the alkali cation is reduced, the solids content increases, and collision and agglomeration of silica particles takes

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Water solutions of alkali silicates are commonly used binders in zinc-rich inorganic coatings. Some colloidal dispersions of silica can also be used as binders. Depending on the alkali used for the solution of the silica or the colloidal dispersion and the ratio of alkali to silica, these coatings have been classed as either self-curing or requiring a post cure to achieve an acceptable degree of water resistance in approximately 8 hours.

Examples of these coatings, which are commercially available, are a sodium silicate solution requiring a post curing treatment such as 10% phosphoric acid in water and a sodium-lithium silicate solution which is classed as self-curing, each being used with zinc. The different cure characteristics of these two coatings are that the former requires about one month's exposure to the atmosphere before it will resist a heavy rain while the latter will resist a heavy rain after only about eight hours' exposure to the atmosphere depending on the ambient temperature and humidity. Therefore, in a relative sense, the sodium-lithium vehicle is self-curing.

However, in practice, especially in the marine industry which is a major user of these inorganic zinc-rich coatings, weather conditions are such that the coating must become completely resistant to rain, fog or extended periods of drizzle in a matter of only

one or two hours after application and under less than desirable conditions such as 50°F. and 70—80% RH (relative humidity).

Under these adverse conditions, currently available, self-curing systems redissolve, causing failure of the coating and requiring reblasting and recoating. To avoid this problem, many users of these water based inorganic coatings have changed to using the solvent based ethyl silicates because they cure by absorbing moisture from the air. U.S. 3,320,082, 3,180,746, and 3,130,061 are relevant prior art patents. However, the fire hazard and toxicity of the solvents are disadvantages.

It has now been found that, unexpectedly, water-based silica- or silicane-containing binders used with a metal such as zinc powder as a protective coating can be made moisture resistant within two hours after application if compounded with certain proportions of an ammonia stabilized colloidal silica.

To solve the problem indicated above when using a water-based material, it was conceived that if a mechanism could be found which would initiate polymerization of the silicate solution as soon as the water evaporates, then a polymer of sufficient molecular weight would develop rapidly, within an hour or two, which would resist all conditions of early exposure down to 40°F.

Polymerization of silicates and colloidal silica increases as the pH drops until it reaches a maximum for most systems at a pH of 5—6. Alkali silicate solutions usually have a pH in the range of 10.5—11.5 due to the presence of fixed alkalis such as sodium, lithium or potassium.

As the system dries upon evaporation of the water, mobility of the alkali cation is reduced, the solids content increases, and collision and agglomeration of silica particles takes

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place. As the alkali is neutralized by absorption of CO_2 from the air or slowly removed from the film by leaching from condensation, fog or rain, the silicate particles become more acidic and the crosslinking reaction with the metallic dust and polymerization process begins. The polymerization continues until a tightly crosslinked film is obtained. Rapid polymerization can be achieved by neutralizing the alkali immediately by post curing with a 10% solution of an acid such as phosphoric. This is the current recommendation for rapidly attaining water resistance.

It is theorized that the polymerization of silicates takes place through the mechanism of a silicic acid intermediate which immediately condenses with silanol hydroxy groups on adjacent silica particles forming siloxane bonds ($\text{Si}-\text{O}-\text{Si}$) thus forming a densely crosslinked SiO_2 polymer which becomes completely water insoluble at very low molecular weights. Thus, the more rapid the rate of polymerization, the faster desired water insensitivity of the coating is achieved.

It is one of the advantages of this invention that a water borne silica or silicate vehicle is provided which will attain a state of complete water resistance within as little as one hour after application without the use of any post curing chemicals such as acid solutions, acid salt solutions, heavy metal salts or high temperatures. Thus, such a further step, which involves additional time and labor, is avoided.

A further advantage of this invention is in providing a water borne silica or silicate vehicle which will form coatings achieving such an early resistance to water, without a loss in shelf life compared with existing water based products.

An additional advantage of this invention is that the metal-rich water based coatings will develop water resistance even at low temperatures (50°F.) within as little as one hour of application, to rain, fog or condensation with or without the use of the above-mentioned commonly used curing agents while still retaining at least five hours' pot life after the metallic dust is mixed with the vehicle.

The water resistant vehicle of the invention is not limited to application to various metals, but may also be used as a clear sealer, adhesive, impregnant for wood or paper and as a binder for ceramics or castings in the foundry trade.

The prior art discloses the use of the silicates of fixed alkalis such as sodium, potassium, lithium or quaternary ammonium silicates or mixtures thereof. The prior art also discloses the use of alkali stabilized colloidal silicas which differ from the silicates in that they are generally considered to be truly colloidal rather than ionic in nature.

As pointed out by Harman (J. Phys., Chem., Volume 31, 616-625; 1927) yellow silicomolybdic complex acid is formed by the

reaction of molybdic acid with ionic silica but not with colloidal silica. Polymeric silica such as is present in colloidal silica dispersions does not give this colorimetric reaction and thus this reaction can be used to distinguish between colloidal silica and ionic silicate solutions such as are mentioned above.

The above silicates and colloidal silicas previously disclosed in the art all suffer from the same basic problem of water sensitivity after application. Although the degree of sensitivity may vary from a few days to several weeks, the practical goal of obtaining a truly water resistant coating in one hour or less based on water borne silica or silicate vehicles has not been achieved without the use of post curing acid solutions, salts, etc., mentioned above.

The only alternative has been the self-curing non-aqueous based solvent borne vehicles such as the ethyl silicates. These become water resistant 20 to 30 minutes after application. By water resistant is meant resistance to rain, high humidity, spray, condensation or fog, particularly the last two. Present systems of the art based on water borne silica or silicate vehicles will not resist fog or condensation until they have dried for several days in most instances.

In accordance with this invention a liquid composition useful as a vehicle from which especially fast-curing water-resistant coatings can be obtained which comprises water and based on the total weight of water and solids, 10 to 45 weight percent of solids comprising:

A. From 10 to 60 weight percent solids of fugitive ammonium ion stabilized colloidal silica based on total SiO_2 (silica) content on a solids basis from both colloidal silica and silicates in said composition;

B. The 90 to 40 weight percent balance of SiO_2 (silica) solids comprising silica or silicate containing material which is

- 1) an organic quaternary ammonium silicate;
- 2) an alkali stabilized colloidal silica;
- 3) a. potassium silicate
b. lithium silicate, or
c. sodium-lithium silicate (as herein-after defined) or

4) a mixture of the foregoing.

A composition capable of fast curing to water resistant coatings comprises 10 to 50 weight percent of this liquid composition and 50 to 90 weight percent of metallic dust capable of entering into polymerization with and becoming part of the SiO_2 polymerized network, the percentages being based on the total weight of said liquid composition and metallic dust.

A thin, dry water resistant protective film from a wet film within 2 hours of wet film formation can be made by applying this composition to an appropriate substrate to form said wet film, drying under ambient conditions to permit the rapid removal of the fugitive ion from said film and thereby effecting a rapid

reduction in the pH of the coating and a concomitant rapid formation of a cross-linked water-resistant film and wherein said ambient conditions include the normal amount of CO₂ in the air which tends to neutralize remaining non-fugitive quaternary ammonium or alkali metal components in the film.

Thus, the present invention includes the following aspects:

- 10 a) a novel water-based alkali-silica/ammonia stabilized colloidal silica binder compositions and;
- b) the new fast forming water resistant coating compositions utilizing the binder composition of a) with zinc dust.

The binder component of the moisture resistant, fast self-curing coating compositions of this invention comprises a critical combination of a silicate or colloidal silica and a fugitive ammonium ion stabilized colloidal silica. It has been found that when the silicate solution or the colloidal silica is combined with the proper ratio of a colloidal silica stabilized with the NH₄⁺ ion, binder vehicles are formed which have excellent shelf life, pot life of 5 hours or more when mixed with metallic dust, e.g. zinc dust, pigment, and that films of these metal-rich coatings have unusually rapid self-curing properties. These formulations provide water- and moisture-resistant films with excellent corrosion resistance in as little as one hour after application.

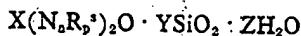
The alkali metal or quaternary ammonium silicates or sols preferably have silica contents of from 10 to 60%, particularly 15 to 50% and especially 15 to 40% by weight.

The sodium-lithium silicate is defined as a silicate in which the molar ratios are from 2.5 to 5.0 SiO₂, from 0.75 to 1.00 Li₂O and from 0.05 to 2.5 Na₂O. Details of the sodium-lithium silicate solution are described in U.S. Patent 3,180,746.

Suitable organic quaternary ammonium silicates include alkylethanol ammonium silicates such as methyltriethanol ammonium silicate, tetraethanol ammonium silicate, diethanol morpholinium silicate, and hexaethanol-ethylene diammonium silicate, dissolved in an aqueous medium. The mole ratios of silica to organic ammonium ion may vary from 1.0 to 20.0, preferably 5 to 20, more preferably 5 to 15.

THE ORGANIC QUATERNARY AMMONIUM SILICATE BINDER COMPONENT — GENERAL FORMULAE AND SPECIFIC COMPOUNDS

It is postulated that the organic quaternary ammonium silicate binder component which can be used can be broadly characterized by the formula:

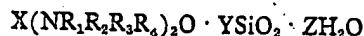


wherein:

N represents a nitrogen atom;
n is a small integer, less than 10 and preferably less than five; X, Y and Z represent numbers defining the relative amounts of each of the component parts of the compound. X is 1, Y is preferably between 0.5 and 20, and Z is preferably between 0 and 99; R represents alkyl radicals containing from 1 to 20 carbon atoms, at least two of which are omega hydroxy alkyl groups (preferably two or more of these R groups are ethanol groups and other derivatives of ethanol groups), up to four groups are associated with each N; p is at least 4, indicating total R groups; and

s is an integer from 1 to p, indicating the number of different types of R groups.

More specifically, the organic silicate binder components useful in connection with this invention can be characterized by the formula:



wherein N, X, Y and Z have the meanings given above and R₁, R₂, R₃ and R₄ represent alkanol radicals containing from 1 to 20 carbon atoms.

PREPARATION OF THE SILICA OR QUATERNARY AMMONIUM SILICATE COMPONENTS OF THE BINDER COMPOSITIONS OF THE INVENTION

The silica or silicate components of this invention may be prepared in a number of ways. Such methods include, for example:

- (a) Removing the alkali metal ion from alkali metal organic ammonium silicates by use of a suitable base exchange resin;
- (b) Dissolving sodium-free silica in sodium-free hydroxylated organic ammonium silicates;
- (c) Dissolving sodium-free silica in sodium-free tetraethanolammonium silicate solutions;
- (d) Leaching sodium from the less soluble sodium quaternary ammonium silicate crystals;
- (e) Reacting ammonia and ethylene oxide with finely divided silica hydrate or silica gel, or a colloidal silica sol.

CONCENTRATION AND SiO₂ CONTENT OF COMPONENTS OF BINDER FORMULATIONS

Aqueous solutions of binder components are preferably prepared with mol ratios of silica to organic quaternary ammonium ion as high as 20, or even greater, and containing 50% by weight or more of SiO₂. The upper limit of concentration depends on the consistency of

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- the final mixture desired and the point at which precipitation or gelation of the final mixture occurs.
- 5 A typical commercially available organic quaternary ammonium silicate which can be used in this invention is Quram 220 or a blend of Quram 220-sodium silicate (1:1 by weight). (The word Quram is a registered Trade Mark).
- 10 Potassium silicates commonly used in the trade with $\text{SiO}_2/\text{Me}_2\text{O}$ ratios of 2.0—4.0 by weight and 20% to 30% by weight SiO_2 were also tested with the ammonia stabilized colloidal silica in a zinc-rich coating. These compositions were not as water resistant as the sodium-lithium silicates tested but were far superior to compositions containing only potassium silicate and zinc dust with no ammonia stabilized colloidal silica.
- 15 Sodium-lithium silicates are most preferred. Lithium silicates are next in order of preference. Sodium silicates are unacceptable for this application, since they do not become water resistant until the level of ammonia stabilized colloidal silica becomes so high that the system becomes unstable when zinc dust is added because the entire system sets up within a few minutes after the zinc is mixed in.
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- 30 The preferred ammonium ion stabilized colloidal silica sol used in this invention is an aquasol containing 20—40 wt% SiO_2 with an SiO_2/NH_3 ratio of 100 to 150 by weight and containing less than 0.1 wt% alkali metal ions.
- 35 Methods of manufacture and composition of these aquasols are described in U.S. Patent 2,574,902. The invention is further illustrated by the following Examples.
- 40 A series of silica-containing compositions was prepared, as follows in which all parts and percentages are by weight.

Example 1. Alkali Metal Silicate Solution

	Parts by Weight
45 Water	52.0
Amine treated bentonite clay	0.5
Sodium alkyl-aryl sulfonate (45%)	2.0
Carboxylated styrene-butadiene latex (45%)	82.0
Alkali metal silicate solution (27%)	415.0
Ammonia stabilized silica aquasol (30%)	415.0

	Parts by Weight
55 Water	434.0
Amine treated bentonite clay	0.5
Methyltriethanol ammonium silicate (50%)	88.0
Sodium silicate solution (37%)	237.8
Ammonia stabilized silica aquasol (30%)	122.0

Example 3. Colloidal Silica Sol-Lithium Stabilized

	Parts by Weight	Example 3.
Water	18.0	65
Amine treated bentonite clay	0.5	
Colloidal silica-lithium stabilized	916.0	70
Carboxylated styrene-butadiene latex (45%)	82.0	
Sodium alkyl-aryl sulfonate	2.0	
Ammonia stabilized silica aquasol (30%)	83.0	

Example 4. Alkali Metal Silicate Solution

	Parts by Weight	Example 4.
Water	52.0	
Carboxylated styrene butadiene latex (45%)	82.0	75
Potassium dichromate (0.1%)	0.6	
Alkali metal silicate solution (27%)	622.0	
Ammonia stabilized silica aquasol (30%)	208.0	
Amine treated bentonite clay	0.5	85

Example 5.

Vehicle of Example 1	100.00
Zinc Dust	326.00

Example 6.

Vehicle of Example 2	100.00	90
Zinc Dust	326.00	

Example 7.

Vehicle of Example 3	100.00
Zinc Dust Powder	326.00

Example 8.

Vehicle of Example 1	100.00	95
Red Iron Oxide Pigment, 0.2—0.5u	100.00	
Natural Calcium Carbonate, 20—40u	16.00	100

The compositions of Examples 1 to 4 result in a silica dispersion which is unique in physical characteristics, appearance and chemical reactivity. When the ammonia stabilized colloidal suspension is added to the indicated ionic silicate solution or colloidal silica sols, an immediate reaction occurs and the reactants change from opalescent, translucent or clear solutions to a milky opaque dispersion of what appears to be a high molecular weight polysiloxane having a large particle size compared with silicate solutions or sols that require the use of surfactants and/or suspending aids to keep them in suspension. The latex further assists this suspension but more importantly allows the system to adhere continuously to very smooth surfaces such as non-sandblasted steel, polished steel, glass, smooth concrete or the like. Surprisingly, the use of reactive type latices, which contain hydroxyl or carboxyl functional groups, does not impair solvent re-

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sistance of the zinc-rich coatings which are frequently used as anti-corrosive linings for solvent tanks or ocean going crude oil tankers. The concentration of these reactive latices should be between 0% and 30% by weight of the composition of the liquid vehicle, otherwise softness, slow cure rates and water sensitivity may result.

Example 9.

An especially preferred binder composition is prepared from the following ingredients:

Material	Pounds	Oz.	Gallons	% By Weight
A Water	133		16.03	5.49
B Bentone (registered Trade Mark)	1	4	0.06	0.05
C Sodium Alkyl Aryl Sulfonate	5		0.43	0.21
D Carboxylated Styrene Butadiene	210		25.30	8.67
E Sodium-Lithium Silicate	1765		177.91	72.88
F Ammonia Stabilized Silica	305		30.50	12.59
G Defoamer (2,4,7,9-tetramethyl-5-decyne-4,7 diol)	2	8	0.31	0.11
Total Charge	2421	12	250.24	100.00

A typical preferred procedure for preparing a preferred binder composition of the invention using the materials indicated above, is as follows:

1. Add A to 55 gallon drum. Start mixer and add B. Stir 10 minutes.

2. When A and B are homogeneous, add C and D in that order with agitation.

3. When C and D are completely stirred in, pour into 260 gallon vat. Add E at a rate of 10 gal./min. with agitation, just making a vortex.

4. When all of E has been added, add F at 10 gal./min.

5. Stir 10 minutes after addition of F is complete and add G. Stir 5 minutes and submit sample to Control Lab for check of specifications.

6. When approved, filter through 80 (U.S. Standard) mesh silk sack. In general this procedure was followed to prepare all the above examples.

The typical specifications on this binder will be as follows: Wt./Gal. @77°F. (Min.) 9.51 — (Max.) 9.81. Krebs Units Vis. @77°F. (Min.) 65 — (Max.) 75 (Stormer Viscosimeter). A coating composition was formulated from 100 g of this binder com-

position and 325 grams of a commercial zinc dust having a mean particle size of from 7—9 μ .

This formulation was applied to an experimental test panel in a wet film thickness of 6 to 10 mils.

The wet film was allowed to dry and formed a hard, dry, adherent film in about 2 hours.

At the 2 hour point, the panel was placed in a 100% fresh water humidity cabinet for 24 hours. The film was then examined. No dissolving of the film was observed after being subjected to this rather severe humidity test.

In order to further illustrate the invention, some of the compositions of preceding Examples as well as newly formulated compositions were evaluated and compared with prior art compositions.

The formulations of these compositions is detailed in Table I in which the amounts are given in parts by weight unless otherwise indicated. The performance of these compositions, particularly with regard to water resistance of the resultant coatings is summarized in Table II.

Table I and Table II are as follows:

TABLE I
**Colloidal Silica Substitutions in Water
 Resistant Formulations**

	A	B	C(1)	D(2)	E	F	G	H	I	J	K
Bentonite	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Water	52	52	52	52	52	52	52	52	52	52	53
Carboxylated Styrene- butadiene latex (45%)	82	82	82	82	82	82	82	84	87	84	84
Sodium alkyl-aryl sulfonate (45%)	2	2	2	2	2	2	2	2	2	2	2
Sodium Silicate (37%)									102		
LUDOX AS-Ammonia (30% SiO_2) stabilized colloidal silica	83	208	415	622	747	830	122			122	
LUDOX 48-Lithium Stabilized colloidal silica (28% SiO_2)											76
Sodium-Lithium Silicate (27%)	830	747	622	415	208	83		706**	732**	706**	706
Defoamer	1	1	1	1	1	1	1	1	1	1	1
IPA Amine											113*
Urea											69*
Totals	967.5	967.5	967.5	967.5	967.5	966.5	967.5	979.5	979.5	922.5	1081.5
Sodium-Lithium Silicate Level	100%	90%	75%	50%	25%	10%					

*Monoisopropanolamine .514% Based on Solids
 Urea .31.16% Based on Solids
 Vehicle to zinc dust ratio:
 1.00/3.26

**Latex added
 (1) Example IV. (2) Example I

(The word 'Ludox' is a registered Trade Mark).

TABLE II
Properties of Colloidal Silica Modified Water Resistant Formulations

Run	Hardness 6 Hr. @ 50°F. -50% RH	Adhesion to Face of Q Panel	Resistance to Redissolving (6 hrs. @ 50°F. -50% RH, then 18 hrs. @ 100°F. RH)	Recovery After 100% Humidity Cycle (24 hrs. @ Room Temp.)	Methanol Resistance (Immersed)	% NH ₃ Stabilized Colloidal SiO ₂ based on total SiO ₂
A	2H	0	3*	4-5*	10	0.0
B	2H	8	3	5	10.56	27.00
C	H	7	7-8	6	-	52.64
D	Gelled	6	7	8-9	-	76.88
E	Gelled	-	-	-	-	90.90
F	Gelled	-	-	-	-	100.00
G	3H-4H	8	8	7	10	16.15
H	4H-5H	9	3	3-4	0.00	0.00
I	3H-4H	8	6	7	2	16.15
J	B	7	9	10	10	0.00
K	H-2H	10	10	10	10	0.00
L	Ethyl-Silicate	Complete Loss of adhesion	3	4-5	10	0.00
Sodium-Lithium Silicate	3H	3	3	3	10	0.00
Sodium-Lithium Silicate-Latex	3H	10	10	10	10	0.00

*Notes

10 = perfect, 1 = complete failure

Samples B-J (except H) were not checked for solvent resistance.

		Parts by Weight Optimum	
5	As can be seen in the above Table II, the films resulting from coatings formulated according to the Table I formulations with zinc dust in a ratio of 1 part of binder formulation and 3.26 parts of zinc dust were tested with various results. The E, F and G systems were so reactive with the zinc that the coating compositions gelled and were ineffective. This is an illustration of the basic difficulty with the use of ammonia stabilized colloidal silica which the art says not to use as is taught in U.S. Patent 3,320,082.	Vehicle (26% NVM) 33 Metallic dust 67	23.4 76.6
10			20 80
15	The essence of the present invention is in finding a way of utilizing the reactivity of the ammonia stabilized system in such a manner that rapid cures (within two hours) can be accomplished, without encountering the over-reactivity problem normally seen with the ammonia stabilized colloidal silica.		100.0
20	It will be noted that in Table II organic system L, which is an ethyl silicate based formulation, performs excellently. Composition K which is a composition of the invention comprising additional amine and urea components also performs almost as well as the organic solvent based silicate.	Zinc preferably has a particle size of from 2 to 50 microns in diameter. Zinc may be added in an amount from 66% to 80% by weight of the coating composition, and the coating compositions will impart increasing corrosion resistance to metal, especially carbon steel, as the amount of zinc is increased.	75
25	In composition I, upon inclusion of a sodium silicate with the ingredients shown, the resistance to water and humidity becomes quite poor. However, upon inclusion of an ammonia stabilized colloidal silica, as in composition H, the resistance to water and humidity is quite good, although not quite as good as for composition K.	In addition to the composition previously discussed, certain other materials, generally referred to as pigments, may be added singly, collectively, or in various combinations to impart certain desired properties to the coating compositions. Several of these "pigment additives" and the desirable characteristics they provide are as follows:	80
30	Compositions C and B also contain quantities of ammonia stabilized colloidal silica; in the case of composition B, the amount is insufficient to give outstanding properties. In the case of composition C, the amount of the ammonia stabilized silica is too large to be optimum.	(1) Inorganic ceramic pigments (metallic oxides which alone or in various combinations yield desired colors) — Example of the metallic oxide pigments are cobalt/aluminum, cobalt/chrome, cadmium, and cadmium/aluminum. The preferred pigments are those commonly used in tinting ceramics.	85
35	The coating compositions of the instant invention are usually packaged as a two-component system. The metallic, e.g. zinc, dust and any other solid pigment used in the coating composition is packaged as one separate component. The vehicle of the present invention together with any other liquid additives is packaged as a second component. The two components are mixed prior to the application of the mixture to the desired surface.	(2) Zinc oxide pigment — Enhances the abrasion resistance and overall "smoothness" of the coating surface by contributing comparatively minute (0.1—1 micron diameter) particles to the coating formulation.	90
40	Since the coating compositions of this invention become water-insensitive within an extremely short period of time, i.e., within two hours, they do not ordinarily require the use of a curing agent. However, in some exceptional cases curing agents such as phosphoric acid can be used to accelerate the cure when exceptionally adverse circumstances are encountered.	(3) Aluminum silica-phosphate pigment — Performs the same function as zinc oxide.	95
45	To the vehicles of the present invention is added metallic, e.g. zinc, dust to form metal-enriched coating compositions. The vehicles and metallic dust are formulated in accordance with the following general formula:	(4) Titanium dioxide pigment — In addition to enhancing the abrasion resistance of the coating, titanium dioxide contributes the excellent hiding properties (brought about by a very high index of refraction).	100
50		The coating compositions of the present invention may be applied to metal surfaces which have been prepared by commercial sandblasting techniques or by wire brushing. The sandblasting need only remove loose mill scale and rust, and the surfaces need not be sandblasted to white metal as is required for the commercially available prior art zinc-rich inorganic coating compositions. The coating compositions may be applied to the surface by brushing, rolling or spraying to obtain a dry film thickness of 1 to 12 mils in thickness. To obtain a preferred dry film thickness, a wet film of 6 to 10 mils of the coating composition is applied to the surface.	105
55		Colloidal silicas are commercially available such as LUDOX 48 which is a lithium stabilized colloidal silica obtainable from the duPont Company. Other commercial sources	110
60			115
65			120
			125

	As can be seen in the above Table II, the films resulting from compositions with zinc dust in a ratio of 1 part of zinc dust to 1 part of total weight, thus, the vehicle when expressed as 26% NVM, means 26% non-volatile materials or total solids.	Vehicle (26% NVM)	33	23.4	20	67	76.6	80	100.0	70
5	Laton and 3.26 parts of zinc dust were reacted with various resins. The R, F and G systems were so reactive with the zinc that the coating compositions gelled and were ineffective. This is an illustration of the basic difficulty with the use of ammonia stabilized colloidal silica.									
10	U.S. Patent 3,200,082, which the art says not to use as is taught in finding a way of utilizing the reactivity of the ammonia stabilized system in such a manner that rapid cures (within two hours) can be accomplished, without encountering the over-reactivity problem normally seen with the ammonia stabilized colloidal silica.									
15	The essence of the present invention is in finding a way of utilizing the reactivity of the ammonia stabilized system II organic amine stabilized colloidal silica.									
20	It will be noted that in Table II organic ammonia stabilized colloidal silica.									
25	In composition I, which is an ethyl silicate with the ingredients shown, the restance to water and humidity becomes quite good, although not quite as good as for composition K.									
30	Compositions C and B also contain quan-									
35	tinum of ammonia stabilized colloidal silica; in the case of ammonia stabilized colloidal silica, in the case of composition B, the amount is in-									
40	venation are usually packaged as a two-com-									
45	ponent system. The metalic, e.g., zinc, dust									
50	venation become water-insensitive within an extremely short period of time, i.e., within a few hours, they do not ordinarily require the use of a curing agent. However, in some ex-									
55	ceptional cases curing agents such as phos-									
60	phoric acid can be used to accelerate the cure when exceptionally adverse circumstances are encountered.									
65	To the vehicles of the present invention is added metallic dust in accordance with the following general formula:									

2. A composition capable of fast curing to water resistant coatings comprising
- 5 I. 50 to 90 weight percent of metallic dust capable of entering into polymerization with and becoming part of the SiO₂ polymerized network;
- 10 II. 10 to 50 weight percent of the composition according to claim 1, the percentages being based on the total weight of components I and II.
- 15 3. A composition according to claim 2 wherein said metallic dust is zinc.
- 20 4. A composition according to claim 2 wherein said metallic dust is aluminium.
- 25 5. A composition according to any one of claims 2 to 4 wherein pigments are also included.
- 30 6. A composition according to any one of claims 2 to 4 wherein the average particle size of said dust is from 5 to 15 microns.
7. A wet, supported film of the composition according to any one of claims 2 to 6 having a thickness of 6 to 10 mils.
8. A dry, water-resistant adherent film formed from the film according to claim 7 after drying.
9. A process for the formation of a thin, dry water-resistant protective film from a wet film within two hours of wet film formation which comprises
- 30 A. Preparation of the silicate or colloidal
- silica solids in aqueous fugitive ammonium ion stabilized system to form the composition according to claim 1;
- B. Blending said composition with 90 to 50 weight percent of metallic dust capable of entering into polymerization with and becoming part of the SiO₂ polymerization network based on the mixture to form the composition according to any one of claims 2 to 6;
- C. Applying said composition to an appropriate substrate to form said wet film, drying under ambient conditions to permit the rapid removal of said fugitive ion from said film and thereby effecting a rapid reduction in the pH of the coating and a concomitant rapid formation of a crosslinked water-resistant film and wherein said ambient conditions include the normal amount of CO₂ in the air which tends to neutralize remaining non-fugitive quaternary ammonium or alkali metal components in the film.
10. A composition according to either of claims 1 and 2 substantially as described with particular reference to the foregoing Examples.

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